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Conversion of Sugar Cane Molasses to 5-Hydroxymethylfurfural Using Molasses and Bagasse-Derived Catalysts

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ABSTRACT: 5-hydroxymethylfurfural (HMF) is a suitable platform chemical for the production of useful chemicals and fuels. This study examined the hydrolysis of mixtures of sucrose, glucose and fructose (synthetic sugar cane molasses) and industrial molasses using sulfonated carbon-based heterogeneous catalysts derived from sugar cane bagasse (B-SO_3H) and sugar cane molasses (M-SO_3H). Microwave heating at 150 °C for 4 h produced 39 mol% HMF yield with B-SO_3H on the synthetic sugar solution. The addition of a molasses pretreatment step, as well as, increasing the microwave power was necessary to achieve similar HMF yields with the industrial molasses sample. The hydrolysis of molasses pretreated with formic acid or HCl resulted in a slightly higher HMF yield than the hydrolysis of molasses pretreated with H_2SO_4. The buffering capacity of the formic acid pretreated molasses was lowered through dilution with water; and subsequently HMF yield was increased to 64.3 mol% (170 °C, 3 h).

INTRODUCTION

Fossil resources derive dominant amounts of energy, synthetic products and chemicals for consumers worldwide[1-2] because of low product cost and ready availability. Unstable crude oil prices and increasingly environmental impacts, such as rising CO_2 levels[3] and propagation of unsustainable levels of non-biodegradable plastics, have helped drive the push towards more sustainable ecological economies. Of the many alternatives for “green” energy production (*e.g.*, solar), biomass is the only suitable “green” reservoir of fixed carbon.[4] Subsequently, there is current significant research interest in the production of fuels and chemicals from renewable biomass resources.

There are numerous chemicals that can be produced via thermochemical processing of biomass. A promising target is the production of high energy density l organics, such as 5-hydroxymethylfurfural (HMF) and furfural,[5-6] 5-chloromethylfurfural,[7] 5-bromomethylfurfural,[8] ethoxymethylfurfural,[9] furandicarboxylic acid and levulinic acid.[10] HMF is a versatile platform chemical due to comprising of three constituent functional groups including a hydroxymethyl (alcohol), formyl (aldehyde) and furan ring groups. These three moieties present ready potential for further conversion and derivatisation. The hydroxymethyl group which is connected to a furanic ring is functionally and structurally similar to benzyl or furfuryl alcohol and hence can easily undergo oxidization (*i.e.*, aldehyde formation), esterification/etherification, and substitution reactions. As a consequence of these attributes, HMF is a key building block chemical for the production of a range of essential products including fuels and chemicals.

The synthesis of HMF from agricultural residues provides an avenue to generate additional revenue for agricultural industries, while negating environmental issues and limiting the reliance on fossil-based resources. The sugar cane industry has large quantities of accessible and available renewable resources. Worldwide, > 1.8 billion tonnes of sugar cane is processed yearly to produce ~250 million tonnes of sugar and a similar amount of residual fibre. Approximately 40 million tonnes of molasses (> 40% sugar content) is also generated in the manufacturing process, which is used for ethanol manufacture and animal feed production. The development of thermochemical methods to produce higher value commodities such as furanics from the carbohydrates found in molasses could provide additional revenue streams to the sugar cane industry.

Numerous articles have reported the use of heterogeneous catalysts for HMF production from the hexose sugars,[11] due to the ease of the catalyst separation and recyclability.[12] It is advantageous to use sustainable and cheap materials to produce these solid catalysts, as well as, inexpensive “green” solvents to enhance the conversion process. The work by Ranoux and co-workers on the autocatalytic conversion of C-6 sugars to HMF, does not require the use of additional catalysts and uses water as solvent medium.[13] While this approach represents a sound option to produce HMF, it necessitates reaction under relatively high temperatures, and relatively high proportions of levulinic and formic acids are also formed, which are not desirable.

Sulfonated amorphous carbon derived from biomass has been used to catalyse HMF production from C-6 sugars.[14] High HMF yields are generally obtained with these catalysts when used in combination with ionic liquids and/or organic solvents or within biphasic systems, although the use of these reaction media may increase the cost of industrial applications. Sulfonated-based carbon catalysts obtained from sugar cane molasses and bagasse have previously been examined for the production of biofuels from algae through the esterification of fatty acids.[15-16] These catalysts have not been studied for the conversion of sugar-based mixtures of feedstocks (*e.g.*, industrial sugar cane molasses) to HMF. Consequentially, this study examined the conversion of synthetic molasses and sugar cane industrial molasses to HMF with microwave heating and catalysts derived from the sugar manufacturing by-products – molasses and bagasse. The effect of molasses pretreatment using HCl, H_2SO_4 and formic acid prior to hydrolysis was also examined. Possible benefits of this pretreatment include; the removal of non-carbohydrate impurities, a reduction in viscosity and improved surface contact with solid catalysts. The catalytic activity of formic acid for HMF production was further studied under various operating conditions, and the effect of molasses dilution on HMF yield was also evaluated.

EXPERIMENTAL

Materials

Sugar cane bagasse and molasses were obtained from Racecourse Sugar Mill in Mackay, Queensland, Australia. The bagasse sample was dried to constant weight at 45 °C, sized using a cutter grinder (Retsch SM100, Retsch GmBH, Germany) before being passed through a 2.0 mm aperture screen. The bagasse sample consists of glucan (43.0 wt%), xylan (17.4 wt%) and lignin (21.5 wt%). These values are similar to published works.[17]

The major constituents present in molasses are water (26.0 wt%), fructose (12.3 wt%), glucose (11.2 wt%) and sucrose (24.2 wt%). The inorganic ions in molasses were determined by inductively coupled plasma optical emission spectrometry (Vista MPX, Varian Inc., Victoria, Australia) included Al (0.54 mg/L), Ca (960 mg/L), Fe (6.2 mg/L), Mg (740 mg/L), P (86 mg/L), K (3400 mg/L), Si (93 mg/L), Na (62 mg/L) and S (990 mg/L). These values are within the expected range for molasses.[18] A bulk sample of molasses was collected, homogenized and stored at 4 °C.

D-(+)xylose, D-(+)fructose, D-(+)glucose, sucrose, and HMF were analytical grade materials. NaCl and NaOH quality were reagent-grade (Sigma-Aldrich Castle Hill, NSW, Australia). Reagent-grade concentrated HCl (32 wt%), H_2SO_4 (98 wt%), phenolphthalein, acetic acid and formic acid were obtained from Merck (Kilsyth, VIC Australia).

Synthetic molasses solution was prepared by dissolving glucose, fructose, and sucrose in a ratio of 11:12:24by weight in distilled water to give a 67 g/L sugar/carbohydrate solution, typical of industrial molasses.

Catalyst preparation and characterisation

Bagasse/molasses (5 g) was pyrolysed by heating in a co-axial furnace under N_2 at 420 °C for 8 h.[15] The product solid was ground and treated with concentrated H_2SO_4 under N_2 at 150 °C for 15 h.[15] The resulting mixture was then cooled, filtered, and washed many times with hot water (2 L), then dried under reduced pressure for 48 h at 70 °C.

The total acid functional groups (*i.e.*, $–SO_3H$, –COOH and –OH) was determined by back titrating NaOH with HCl.[15] A solution of 20 mL NaOH (0.01 M) was agitated and mixed with 0.05 g catalyst for 1 h. The solution from the mixture was obtained by centrifugation and filtration, and titrated with HCl (0.01 M). The $–SO_3H$ groups were determined by titrating a solution obtained by treating the catalyst (0.05 g) with 20 mL of 0.01 M NaCl solution for 1 h with NaOH using phenolphthalein as an indicator.

The results indicated molasses-based sulfonated carbon catalyst ($M\text{-}SO_3H$) contains 3.98 mmol/g total acid sites (*i.e.*, $–SO_3H$, –COOH and –OH) and 2.01 mmol/g strong acid sites ($–SO_3H$). These values are similar to results for beet molasses-based catalysts.[15] The bagasse-based sulfonated carbon catalyst ($B\text{-}SO_3H$) contained 3.61 mmol/g total acid sites and 1.89 mmol/g strong acid sites similar to what is published in the literature.[16]

The compounds that fouled and hence deactivated the catalysts were analysed by Fourier transform infrared (FTIR) spectroscopy The Infra-red spectra were collected using a Nicote 870 Nexus FTIR system, consisting of a continuum IR microscope equipped with a liquid nitrogen-cooled MCT detector and an attenuated total reflectance, ATR; Nicolet Instrument Corp. Madison, WI).

Molasses treatment

The processing method applied to molasses was similar to that published by Liu et al.[19] In a typical experiment, the molasses was diluted with water to 30% (w/w) total sugar content and then adjusted to pH 3.5 with HCl, H_2SO_4 or formic acid. It was then heated to 60 °C for 2 h. This treatment did not result a noticeable change in the saccharide contents. At the end of the treatment, the solution was cooled centrifuged and filtered, and the resulting solution was diluted to 67 g/L (unless otherwise specified) total sugars and stored at -4 °C. The solids recovered after centrifugation and filtration was washed with distilled water and dried for 12 h, prior to X-ray powder diffraction analysis. The sugar content of solution was analysed by high-performance liquid chromatography (HPLC).

Hydrolysis with microwave

For the microwave (Milestone START SYNTH microwave; Milestone, Germany) hydrolysis trials, 300 mg of catalyst was added to 25 mL of a 67 g/L carbohydrate solution in a Teflon reactor (NOVA-8 vessels of 75 mL capacity). The microwave was heated with 300 W or 500 W power to the required temperature (heating rate of ~50 °C/min) and maintained at the temperature for a specified time.[20] The reaction pressure was estimated to be 480 kPa for a temperature of 150 °C. At completion of the reaction, the solution was cooled, then centrifuged to remove residual solids, and diluted with distilled water. The hydrolysis trials were done in triplicate.

Equation 1 was used to calculate the HMF yield, where HMF (mol) is the HMF quantitated after microwave hydrolysis, while the amounts glucose, fructose and sucrose are that available for hydrolysis before hydrolysis.

$$Yield\ of\ HMF\ (mol\ \%) = \frac{100\ (\%) \times HMF\ (mol)}{[Glucose\ (mol) + Fructose(mol) + 2 \times Sucrose\ (mol)]} \qquad \underline{\textbf{Equ 1}}$$

HMF and sugar analysis

A Waters HPLC system (Milford, MA, USA) with a Bio-Rad Aminex HPX-87H column was used to detect and quantify HMF. The column temperature was set at 65 °C and 5 mM H_2SO_4 at a flow rate of 0.6 mL/min was used as eluent. A Phenominex RPM monosaccharide column (set at 85 °C) was used to determine the concentration of sugars and the eluent was water set at a flow rate of 0.5 mL/min.

X-ray powder diffraction analysis

X-ray power diffraction (XRD) of the solid residue obtained after molasses pretreatment with acid was carried out on a PANalytical X'Pert MPD X-ray diffractometer, using a diffraction camera (Rigaku) with an X-ray generator with Cu Kα radiation of wavelength 1.5418 Å.

RESULTS AND DISCUSSION

Synthetic molasses

Effect of temperature

Several preliminary hydrolysis trials were carried out on synthetic molasses from 110-150 °C for 30 min reaction time using a microwave power of 300 W in order to determine the preferred temperature for HMF formation. In contrast to the literature, little or no HMF was formed at 110 °C.[14, 21] At 130 °C sucrose hydrolysis proceeded but no quantitative amount of HMF was obtained (Table 1). In the presence of acid, sucrose is readily hydrolysed to fructose and glucose under relatively thermodynamically neutral conditions (-5 kcal/mol enthalpy change on ion-exchange resin).[22] The hydrolysis of monosaccharides to HMF has been consistently reported to exhibit higher enthalpy change than that of sucrose hydrolysis at 24 kcal/mol.[23] The reaction conditions at 130 °C were found sufficient for the inversion of sucrose, while formation of HMF was less energetically favourable and occurred at > 130 °C.

Table 1 - Hydrolysis of synthetic molasses solution

Catalyst	**B-SO_3H**		**M-SO_3H**	
Temp (°C)	130	150	130	150
Residual glucose (%)	88.2	94.2	88.2	98.0
Residual fructose (%)	85.9	78.4	85.9	73.6
Total unreacted saccharides (%)	87.1	86.4	87.1	86.0
HMF yield (mol%)	< LOQ	7.6	< LOQ	11.2

LOQ = limit of quantitation

Notes: 25 mL of 67 g/L sugar solution; 300 mg catalyst; 30 min reaction time; 300 W microwave (MW) power; RSD: HMF < 10%, individual sugars < 4%, total sugars < 8%; yield based on hexose sugar content hydrolysed to HMF

Reactions undertaken at 130 °C using B-SO_3H revealed glucose and fructose were consumed in comparable proportions, with little or no HMF formed. Production of non-HMF products could occur due to saccharides undergoing a “caramelisation” reaction (*e.g.*, enolisation, anhydride formation and polymerisation).[24] At 150 °C, HMF is produced in reasonable yields and fructose seems to be selectively consumed because of its primary furanose conformation and lower activation energy[25] compared to glucose. At this temperature, M-SO_3H is more effective than B-SO_3H for the formation to HMF.

The results reported in Table 1 are higher than the 2.5 mol% reported for glucose using sulfonated cellulose in water at 160 °C (conventional heating) for 15 min[26] and 2.3 mol% obtained using sulfonated lignin at 100 °C (conventional heating) for 1 h[21] but lower than the 20-40 mol% yields of HMF obtained for fructose using microwave heating at 150 °C for 1 h with sulfonated lignin and biomass-derived solid catalysts.[14] A number of factors could account for the variation and include differences in the physico-chemical properties of the catalyst and dosage, feed carbohydrate composition, reaction time and temperature, and solvent volume. It has been noted that catalytic activity of these biomass derived catalysts is not only depended on acid density but also the nature of the polycyclic aromatic carbon sheets surrounding the -SO_3H group.[27]

Effect of time

An increase in glucose concentration was observed after 1 h reaction with the use of both catalysts (Table 2). The glucose content of the M-SO_3OH and B-SO_3OH systems decreased after 2 h and 3 h respectively. The existence of increased levels of glucose isomers in solution indicates the isomerisation reaction of fructose to glucose occurs slightly faster than the HMF-producing hydrolysis reaction; which negatively impacts on HMF yield. A maximum yield at 3 h was achieved with M-SO_3H, the more acidic catalyst, whereas the bagasse-based catalyst (B-SO_3H) reached maximum yield at 4 h. A similar drop in yield over long reaction times has been previously reported, both before[13] and after[28] conversion of available fructose. Reduced specificity influences the decrease in yield, possibly due to a number of subsequent HMF reactions such as hydrolysis to organic acids,[13] degradation to humins through aldol addition and condensation reactions,[29] or other degradation pathways.

In all the hydrolysis reactions, a maximum HMF production rate was exhibited in the initial time period (30 min). Under longer reaction times humin production is a known cause of reduced activity that would lead to lower reaction rates.[29] Additionally, irreversible adsorption of furanics onto carbon[30] or acidic sites can deactivate the catalyst sites[31] further reducing reaction rates. As HMF converts to organic acids, the change in concentration and pH will also affect specificity and yield of the target products.[32] Typical HMF hydrolysis products of levulinic[33] and formic acid[32] can act as catalyst and further increase HMF production. Hydrolysis of the carbohydrates (synthetic molasses) was also carried out at 150 °C over 4 h without catalyst as the hydrolysis of saccharides to HMF is also known to be autocatalytic.[13] For these conditions with no catalyst, HMF yield was 18.4 mol% with a specificity of 26% over this period of 4 h. No residual sucrose, glucose and fructose remained at this time.

Table 2 - Hydrolysis of synthetic molasses to HMF at 150 °C and different times

Catalyst	Reaction time (h)	Residual glucose (%)	Residual fructose (%)	Total unreacted saccharides (%)	HMF yield (mol%)
B-SO_3H	0.5	94.2	78.4	86.4	7.6
B-SO_3H	1	102.0	68.0	85.2	14.8
B-SO_3H	2	105.0	46.2	75.9	26.9
B-SO_3H	3	105.0	34.4	71.5	36.9
B-SO_3H	4	101.0	16.7	59.2	39.1
M-SO_3H	0.5	98.0	73.6	86.0	11.2
M-SO_3H	1	103	85.8	81.8	22.0
M-SO_3H	2	109	32.0	70.6	33.9
M-SO_3H	3	93.4	25.1	59.6	34.2
M-SO_3H	4	93.7	8.0	51.3	30.9
None	4	n.d.	n.d	n.d	18.4

Notes: 25 mL of 67 g/L sugar solution; 300 mg catalyst; 300 W MW power, 300 W; 150 °C; RSD: HMF < 10%, individual sugars < 4%, total sugars < 8%; yield based on hexose sugar content hydrolysed to HMF

The results obtained in this study are in agreement with those of Guo et al.[14] for the conversion of fructose to HMF using a lignin-based catalyst (fructose 4 g, catalyst 1 g in 20 mL of water, microwave heating, 150 °C, 1 h), where 39% HMF was produced. However, Guo et al.[14] achieved significantly higher yield with the catalyst in ionic liquid/DMSO combination. It should also be pointed out in the present study a mixture of sucrose, glucose and fructose was used which is less efficiently converted to HMF. This was demonstrated by Guo et al.[14] who reported a drop in HMF yield in ionic liquid/DMSO solvent from 84 mol% (110 °C for 10 min) for fructose to 68 mol% for glucose under more severe conditions (160 °C for 50 min).

Hydrolysis of molasses

The hydrolysis of industrial molasses was also studied by conducting trials for 30 min at 110, 130 and 150 °C with a microwave power of 300 W similar to the synthetic molasses study. The amounts of HMF produced were not quantifiable, in contrast to the synthetic molasses solution. The different components of biomass (including inorganics) have been found to affect microwave energy absorption,[28] and may help explain the inability to promote hydrolysis of molasses at 300 W. Increased microwave power is commonly employed to promote reaction of more robust or recalcitrant samples, such as the hydrolysis of lignocellulosic biomass and cellulose.[28] The rationale cited is that microwave irradiation promotes organic reactions through rapid and efficient heat generation, enhanced substrate interactions[34] and increasing particle collisions.[20] This has the effect of altering chemical reaction pathways and accelerating reaction rates,[28] including the target HMF-producing reaction.[14] The production of non-HMF products under non-microwave conditions is possibly encouraged by the lower heating, allowing saccharides to undergo "caramelisation" (*e.g.*, anhydride formation and polymerisation).[24] The HMF yields from 0.5 h to 4 h using a higher microwave power of 500 W are given in Table 3. The amount of sucrose remaining was found to be 15.1 wt% and 2.9 wt% for the process catalysed with B-SO_3H and M-SO_3H respectively at 30 mins. The solutions came to ~130 °C within 3 mins at 300 W and 150 °C within 3 mins at 500 W. No sucrose was detected with synthetic molasses at 0.5 h with lower microwave power (Table 2). This suggests an overall slowing of the hydrolysis process, more notable with the less acidic B-SO_3H catalyst. The slowing of the hydrolysis process could be related to the physical blocking of the acid sites of the catalysts by both organic and inorganic impurities in the molasses as well as the strong association between sucrose and inorganic components (*e.g.*, calcium) to form saccharide complexes. It is likely that the buffering effect[35] of molasses additionally slowed the hydrolysis process.

The more acidic M-SO_3H showed similar specificity and slightly greater HMF conversion rate than B-SO_3H. In contrast to synthetic molasses, the fastest rate of molasses conversion to HMF did not occur at 0.5 h but occurred around 2 h. The catalyst, M-SO_3H at 4 h reaction time gave a similar result as that of synthetic molasses without a catalyst (Table 2), while the catalyst B-SO_3H gave a slightly lower value for the same heating time. These results further confirm that the non-sugar components present in industrial molasses play an important role in carbohydrate hydrolysis.

Table 3 - Hydrolysis of industrial molasses to HMF at 150 °C at various times

Catalyst	Reaction time (h)	Residual sucrose (%)	Residual glucose (%)	Residual fructose (%)	Total unreacted saccharides (%)	HMF yield (mol%)
B-SO_3H	0.5	15.1	100	89.4	94.7	1.77
B-SO_3H	1	0	87.1	64.2	75.7	4.79
B-SO_3H	2	0	80.5	41.0	60.9	10.9
B-SO_3H	3	0	74.3	28.5	51.4	16.3
B-SO_3H	4	0	69.6	20.3	45.1	17.3
M-SO_3H	0.5	2.94	94.0	80.5	87.3	2.69
M-SO_3H	1	0	87.3	62.7	75.0	6.22
M-SO_3H	2	0	80.7	37.7	62.7	12.9
M-SO_3H	3	0	73.2	26.7	50.0	17.4
M-SO_3H	4	0	62.6	14.8	38.9	18.7

Notes: 25 mL of 67 g/L sugars from molasses; 300 mg catalyst; 500 W MW power; 150 °C; RSD: HMF < 10%, individual sugars < 4%, total sugars < 8%; yield based on hexose sugar content hydrolysed to HMF

HMF production from industrial molasses exhibited markedly lower yields and specificities (compared to the synthetic molasses comprising neat carbohydrates) which may be related to catalyst deactivation and production of higher amounts of degradation products. The industrial molasses reaction matrix contains additional components including lipids, proteins, oligosaccharides and polysaccharides, amino acids, organic acids and phenolics[36] that can take part in or enhance humins formation and also foul and deactivate the catalyst. This may explain the reduced HMF yields in the hydrolysis of industrial molasses solution.

FTIR spectra were obtained for the fresh catalysts and the catalysts after hydrolysis of the molasses solutions (Figure 1) in order to determine differences in the functional group contents on the surface of the catalyst. The spectra were normalised to the aromatic ring stretching vibration peak (1600 cm^{-1}), representative of the carbon support of the catalyst. The spectra show a broad band at 3400 cm^{-1} assigned to O-H stretching, sharp peaks at 1715 cm^{-1} ascribed to C=O stretch in carboxylic acid groups and peaks in the 1200-1000 cm^{-1} range that are both typical of C-O stretching and deformation in phenolic and aromatic groups.[15-16] The fingerprint region (1200-1000 cm^{-1}) is difficult to characterise fully as S=O symmetric and asymmetric stretching vibration peaks (1020-1030 cm^{-1} and 1140-1150 cm^{-1} respectively) that are attributed to the –SO_3H groups incorporated onto the catalyst surface would also be present in this region.[15-16, 27]

In comparison with fresh catalyst, the spent catalyst exhibited new small peaks at 1510 cm^{-1}, 1355 cm^{-1} and 960 cm^{-1} attributed to C-O stretching in furan rings[29] which are due to the deposition of HMF degradation products onto the catalyst surface (Figure 1). Additional peaks at 2920 cm^{-1} and 2840 cm^{-1} were also detected with the spent catalyst derived from the hydrolysis of industrial molasses. These peaks were absent in the spent catalyst derived from the hydrolysis of the neat carbohydrate solutions. These peaks are attributed to CH stretching modes in aliphatic compounds of the attached side chains of protein compounds.[37]

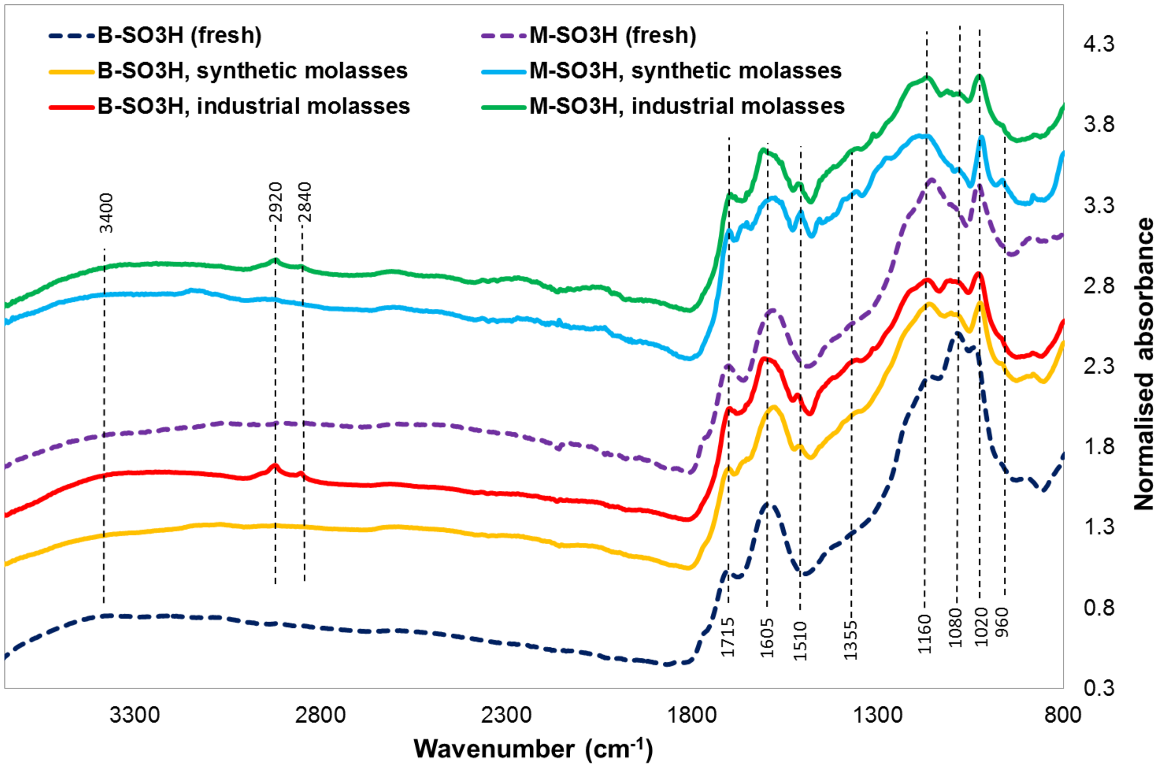

Figure 1 - Normalised FTIR spectra of fresh and used catalysts

Figure 1 also shows broadening of the regions at 1600-1550 cm^{-1} and 1200-1160 cm^{-1} for the spent catalysts. These are attributed to C=C vibrations of deposited condensed organic material. The possible detection of nitrogen (1660 cm^{-1} for amine deformation and 1200 cm^{-1} for C-C-N bending)[37] supports this hypothesis. A shift in peaks of the spent catalysts to lower frequency (*e.g.*, 1715 cm^{-1}, 1020 cm^{-1}) also indicate a more condensed structure is formed and/or increased intermolecular bonding of the species.

Differential FTIR spectra comparing the fresh and spent catalysts were examined to provide a more detailed analysis of the solids deposited on the catalyst surfaces (Figure S1, Supporting Information). The difference spectra show that the solid residue comprises humic substances (with furanic ring structures at 1510 cm^{-1}, 1355 cm^{-1} and 960 cm^{-1}) and protein compounds (amine deformation at 1650 cm^{-1}). The difference spectra also show a reduction in intensity of 1200-1000 cm^{-1} region, which may be caused by the deposition of organic material onto the carboxylic and sulfonated acid sites of the catalyst surface reducing the peak intensity.

The amino acids content in sugar cane molasses (*e.g.*, glycine)[36] can take part in Maillard-like reactions with HMF and lead to the formation of melanoidin polymers.[38] Nitrogen containing melanoidin polymers are similar to humic substances,[39] and would contain smaller amounts of aromatic moieties compared with humic polymers produced from furans.[38] This would produce solids with less-aromatic nature after molasses hydrolysis (Figure S1, region at 1510 cm^{-1}).

Hydrolysis of molasses - Effect of acid pretreatment

Often pretreatment of recalcitrant feedstocks is necessary to enhance r hydrolysis reactions. Here, liquid acid pretreatment was utilised as a relatively simple method to precipitate both inorganic and organic impurities in molasses, while allowing tuning of pH, a crucial factor in minimising undesirable reactions and also acting as a homogeneous catalyst. Three acids were examined for the purification of molasses and increased catalytic activity for the subsequent hydrolysis reaction (Table 4).

Table 4 - Hydrolysis of acid pretreated industrial molasses

Catalyst	Pretreatment Acid	Residual sucrose (%)	Residual glucose (%)	Residual fructose (%)	Total unreacted saccharides (%)	HMF yield (mol%)
None	H_2SO_4	0	85.9	22.8	54.0	23.5
B-SO_3H	H_2SO_4	0	88.9	21.8	55.1	26.6
M-SO_3H	H_2SO_4	0	91.6	18.5	54.7	29.2
None	HCl	0	49.1	52.9	51.0	30.5
B-SO_3H	HCl	0	88.7	20.2	54.4	39.8
M-SO_3H	HCl	0	78.2	18.2	48.2	35.6
None	HCOOH	0	78.5	20.4	49.4	31.4
B-SO_3H	HCOOH	0	82.4	17.1	49.6	39.0
M-SO_3H	HCOOH	0	71.5	13.0	42.2	34.6

Notes: Molasses solution treated to pH 3.5, 25 mL of 67 g/L sugars; 300 mg catalyst; 500 W MW power; 150 °C; 4 h reaction time; RSD: HMF < 10%, individual sugars < 4%, total sugars < 8%; yield based on hexose sugar content hydrolysed to HMF

Sulfuric acid with and without solid catalyst gave the lowest yield and specificity than the other acids (Table 4). The improvements of HCl over H_2SO_4 may be due to the formation of a chlorinated intermediate,[40] which could lower the activation energy for HMF formation.[41] Formic acid is a carboxylic acid, a class of compound that is known to provide synergy in solid acid hydrolysis by altering solvent polarity and improving surface coverage.[42]

The use of solid catalysts with the acid pretreated molasses increased HMF yield by 24-30% compared to the results obtained without the use of the catalyst. B-SO_3H gave a slightly higher HMF yields with HCl and formic acid treatments compared to M-SO_3H, but a lower value with H_2SO_4 treatment. The HMF yield obtained with HCl treated molasses with B-SO_3H is over twice that obtained with same catalyst on untreated molasses. A similar result was obtained for formic acid treated molasses with M-SO_3H.

XRD analysis of the solid residue (Figure S2, Supporting Information) recovered after acid pretreatment indicated that calcium oxalate dihydrate (weddellite) and quartz were the main crystalline compounds present. The signal at $2\theta = 22$ ° indicate a large proportion of amorphous material which is due to organics such as polysaccharides and protein precipitating during the acid pretreatment. These precipitated inorganic and organic compounds may have blocked acid sites on the solid catalysts and hence, to a certain extent, could influence the conversion of molasses to HMF.

Hydrolysis of molasses - Effect of formic acid alone

The results presented in Table 4 show that the use HCl and formic acid gave similar HMF yields. The multiple role of formic acid in pretreatment, catalyst and solvent was investigated (Table 5). Formic acid has good green credentials,[43] and it can be produced with levulinic acid from HMF.[44] Formic acid is also easier to separate chromatographically from carbohydrates than HCl.

A reaction pH of 2.15 provided the maximum HMF yield and specificity and required a concentration of 15% v/v formic acid to achieve due to the buffering effect of molasses. The solvent effect of formic acid on the molasses feedstock has been reported to best facilitate hydrolysis with-in this range.[32] Substantial amounts of liquid catalyst is not preferred due to downstream recovery processing considerations.[12] Therefore, higher solid catalyst loadings with lower formic acid concentration were examined (Table S1, Supporting Information). A HMF yield of 41.8% was obtained at pH of 2.36 (molasses pretreated with 4.4% formic acid). This result is similar to that of the molasses solution containing 15% formic acid, further confirming the benefits derived from using the sulfonated carbon catalysts. In order to see whether HMF yield can be maintained at a lower formic acid concentration with increasing solid catalyst load, the pretreated molasses having a reaction pH of 3.41 (produced by treatment with 0.2% formic acid) was hydrolysed in the presence of M-SO_3H. Increasing the catalyst loading decreased the product yield (Table S1, Supporting Information). The decrease observed could be due to hydrolysis reagents and products binding onto carbon[30] or catalytic sites,[31] leading to lower HMF yields.

Table 5 - Effect of solution pH and formic acid concentration on HMF yield

Pretreatment	Initial reaction pH	Residual sucrose (%)	Residual glucose (%)	Residual fructose (%)	Total unreacted saccharides (%)	HMF yield (mol%)
pH 3.5 (0.2%)	3.41	0	78.5	20.4	49.4	31.4
pH 3.0 (0.5%)	3.38	0	89.1	3.15	45.6	32.9
pH 2.5 (1.1%)	2.99	0	87.1	6.44	46.5	32.8
pH 1.5 (4.4%)	2.36	0	78.9	10.9	44.5	38.4
pH 1.5	2.36*	0	79.8	1.1	39.7	41.8
15%	2.15	0	77.6	0.53	38.2	42.3
20%	1.93	0	78.3	0	37.9	38.9
25%	1.77	0	81.9	0	39.6	38.1

Notes: 25 mL of 67 g/L sugars from molasses; 500 W MW power; 150 °C; 4 h reaction time; RSD: HMF < 10%, individual sugars < 4%, total sugars < 8%; formic acid reported as volume %; yield based on hexose sugar content hydrolysed to HMF, * with 300 mg M-SO_3H

Hydrolysis of molasses - Effect of increased temperature

The hydrolysis process was further examined by increasing the temperature from 150 to 170 °C (Table S2, Supporting Information).

The highest yield (40.8 mol%) and specificity (84%) were observed after 1 h which is of similar magnitude (though lower) than the 40-80% yields reported by others with sulfonated biomass-derived solid acid catalysts under microwave irradiation.[14, 21, 26] It should be noted that the higher HMF yields reported in literature were from fructose and glucose in IL or solvent-assisted systems. The reduction in yield and specificity over time is because of the formation of degradation products which increases in content with harsher conditions. As the highest yield of HMF from molasses was ~41% it was logical to examine whether lowering the molasses buffering capacity through dilution would increase HMF formation. Using a diluted pretreated molasses HMF yield significantly increased yields from 36.2% (Table S2, Supporting Information) to 64.5% for 3 h (Table 6). Reactions with further increase in reaction time were not conducted due to the reduction in selectivity and yield obtained with pretreated molasses for 4 h at 170 °C (Table S2, Supporting Information). Other researchers found that using 1 M phosphate buffer medium, the HMF yield from fructose heated at 190 °C was 4% but increased to 28.5% in 0.1 M of the same buffer.[13] It was suggested that the increase in buffer concentration increased the neutralization of the acid formed insitu, and hence resulted in preferential formation of humins.[13] The dilution of molasses to lower carbohydrate content in this work would invariably have improved surface reactions on the carbon catalysts and improved mass transfer reactions.

Table 6 - Hydrolysis of diluted molasses solutions with M-SO_3H

Reaction time (h)	Residual glucose (%)	Residual fructose (%)	Total unreacted saccharides (%)	HMF yield (%)
0.5	80.9	46.7	64.0	19.0
1	72.7	27.5	50.3	28.8
2	66.4	7.66	37.3	60.3
3	37.5	2.90	20.4	64.5

Notes: 25 mL of 33.5 g/L sugars from molasses; 300 mg catalyst; 500 W MW power; 170 °C; RSD: HMF < 10%, individual sugars < 4%, total sugars < 8%: yield based on hexose sugar content hydrolysed to HMF

CONCLUSIONS

The results have shown that the hydrolysis of sugar cane industrial molasses with sugar cane by-product derived catalysts for HMF formation occur at a far slower rate than that of a solution of neat saccharides (*i.e.*, synthetic molasses) under similar conditions. Molasses not only contain organic acids (*e.g.*, formic acid) but also divalent and trivalent cations and anions (*e.g.*, Cl^-) all of which should auto-catalytically convert the sugars to HMF. These compounds were found not to accelerate or enhance HMF formation. It was found necessary to increase the microwave power and remove some molasses impurities using a simple acid pretreatment step in order to improve HMF yields. The use of acid in combination with the carbon catalysts enhanced HMF formation. Significant improvement in HMF yield was obtained by further diluting the industrial molasses with water. This process lowered the buffering capacity of the system.

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SUPPORTING INFORMATION

FTIR differential spectrum of fresh catalysts subtracted from the spectrum of the corresponding spent catalysts after hydrolysis of the industrial molasses (Figure S1).

XRD analysis of the solid residue recovered after acid pretreatment of industrial molasses (Figure S2).

Effect of catalyst loading on HMF yield from industrial molasses (Table S1).

Hydrolysis of pretreated molasses at 170 °C by M-SO_3H (Table S2).

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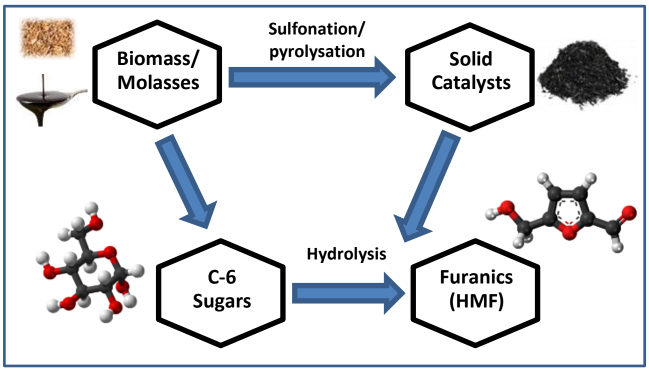

SYNOPSIS: The conversion of molasses, a sugar industry byproduct, to HMF was studied using sulfonated solid catalysts derived from biomass.